Sources and Radiative Impact of Carbonaceous Aerosols Using Four Years Ground-Based Measurements over the Central Himalayas

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ABSTRACT

Climate and health in the pristine Himalayan region are largely impacted by the transport of carbonaceous aerosols from the polluted regions of Asia and Europe. Yet, there is a scarcity of source apportionment studies that can explain diurnal scale phenomena concerning various emission sources and radiative forcing. Here, we report the first simultaneous high-resolution delineation of primary organic carbon (POC) and secondary organic carbon (SOC) content and quantify the contributions of fossil fuel combustion and biomass burning over the Central Himalayas using four-year (2014–2017) online observations. Four different methods are employed to deconvolute organic carbon (OC) into POC and SOC. Unlike SOC, POC exhibits significant unimodal diurnal variations with higher values during daytime in all four methods. These methods show intra-annual variations in POC (56–80%) and SOC (20–44%) concentrations but they agree that overall POC (4.7–8 µg m⁻³) dominates over SOC (2.4–3.9 µg m⁻³). The role of crop residue burning in northern India and forest fires is shown to be dominant in spring while local heating-purpose emissions dominate in winter. Further, we show that the contribution of fossil fuel combustion (eBCff) is 3.5 times greater than that of biomass burning (eBCbb). Monthly variations in mean diurnal amplitudes of eBCff and eBCbb reveal that the differences in their amplitudes (9–32%) is smallest during April–May, depicting the relative importance of biomass emissions at the diurnal scale during spring. The estimated daily radiative forcing shows that eBC ff contributes more (16.4%) atmospheric forcing than eBCbb. Atmospheric forcing from both eBCff and eBCbb are higher (19.8 and 13.0 W m⁻², respectively) in the afternoon than morning. These findings underscore the need for high-resolution data when researching aerosol-radiation interaction over the Himalayan area and are vital for developing aerosol mitigation plans.

Keywords: Organic carbon, Black carbon, SOC, Himalaya, Fossil fuel and biomass, Radiative forcing

1 INTRODUCTION

Carbonaceous aerosols—black carbon (BC) and organic carbon (OC) have a substantial impact on health (e.g., Ostro et al., 2015) and climate (e.g., Zanatta et al., 2016) and constitute a major fraction of particulate matter (Malm et al., 2004). BC absorbs light and is known to be a significant contributor to radiative forcing (~1.1 W m⁻²), especially due to its direct as well as indirect effects on radiation and clouds, in addition to its potential to accelerate snow melting (Andreae and Gelencsér, 2006; Bond et al., 2013). Model simulations (1971–2010) suggested (Sharma et al., 2022) that absorbing aerosols, including BC, induced a significant increase in surface air temperature (0.2–2°C), with higher warming in parts of the Western and Central Himalayas during spring. These estimates of radiative forcing are based on daily averages, and the role of diurnal variations in carbonaceous aerosols is still not known.

Globally, 7.6 Tg of BC is emitted, with 25% contribution coming from diesel combustion, 27% from domestic solid fuel emissions and 40% contribution from biomass burning (Bond et al., 2013).
These fractions significantly vary between urban, rural, and remote environments (Venkataraman et al., 2005). One of the important reasons for uncertainties in the BC emissions and uncertainty in radiative forcing estimates is our inadequate knowledge about the contribution of fossil fuel combustion and biomass burning to the total BC (Rajesh and Ramchandran, 2017; Kant et al., 2020). Such source apportionment studies of BC, using long-term observational data, are especially limited over the Central Himalayas, despite India being the second largest BC emitter in the world (Bond et al., 2013).

BC has only primary sources of emission while OC can have both primary as well as secondary sources of emission (Cabada et al., 2004). The combustion activities such as vehicular emissions, coal burning, and biomass burning emit both BC and primary organic carbon (POC). Secondary organic carbon (SOC) can be formed through volatile organic compounds (VOC), such as monoterpenes, isoprene, β-caryophyllene, and toluene (Kleindienst et al., 2010). While new techniques with online quantification of oxygenated functional groups in SOC exist, a complete quantification of these aerosols is still limited (Wu and Yu, 2016), especially in remote regions. The soot carbon defined by thermal methods, also known as elemental carbon (EC) (Petzold et al., 2013), is widely employed as a tracer to estimate POC due to its co-emission with OC and generation through only primary sources (Cabada et al., 2004; Wu and Yu, 2016; Yoo et al., 2022). The determination of POC and SOC is very limited in the high-altitude Himalayan sites. The studies that are available from the area are either offline or only available for a brief time (Sharma et al., 2020; Kumar et al., 2021; Sheoran et al., 2021; Choudhary et al., 2022). Offline measurements though informative, hide the swift variation of aerosols at the diurnal scale and are subject to biases because of the delay between sampling and analysis, which increases the risk of contamination and artefacts due to the presence of volatile organic compounds. In fact, the only long-term online POC-SOC concentrations available in the Indian region are from highly polluted urban sites like Delhi (Tiwari et al., 2013) and Pune (Safai et al., 2014).

To bridge this gap, online and simultaneous measurements of equivalent black carbon (eBC), OC, EC, and CO were conducted for four years during 2014–2017 at a high-altitude site in the Central Himalayas. Thus, this paper presents the results of source characterization from these observations, which can reveal the diurnal scale phenomenon.

2 OBSERVATIONAL SITE AND METEOROLOGY

The ground-based aerosol observations were carried out at the Aryabhatta Research Institute for Observational Sciences (ARIES), Nainital (29.4°N, 79.5°E, 1958 m a.m.s.l.) in the Central Himalayas. Nainital is a high-altitude site (Fig. 1) and the nearest towns of Haldwani and Rudrapur with a population of about 0.2 million are located about 20 and 40 km south of Nainital, respectively. Both towns host only small-scale industries and those too are non-combustible in nature. The observation site is environmentally shielded by the high-altitude mountains of the Himalayas in its northeast, thus usually preventing pollutant transport from this direction. In the northwest are located the low-altitude mountains of the Himalayan region. The only local sources of pollution are mainly automobiles. The major possible sources of pollution are in the low-lying Indo-Gangetic Plains in the south which is identifiable from Fig. 1(a) as the region with high BC concentrations (MERRA-2 model) depicted using orange and red colours.

Major meteorological parameters recorded at the site during 2014–2017 are shown in Fig. 1(c). The site is influenced by heavy rain during the monsoon period starting from June and lasting till early September and is thus characterised as a wet period. The maximum rainfall occurs in July, registering a mean of 682 mm of rain. Relative humidity is also enhanced around the same period in monsoon with a peak of 97% occurrence in July. The maximum temperature observed at the site is about 20°C during May–June while the winters (DJF) are usually cold and the minimum temperature of ~8°C is observed in January. Due to the overcast conditions during monsoons, the solar radiation goes down to a minimum of ~200 W m⁻² while the maximum solar radiation is received during the spring season (MAM), which rises to a maximum of ~440 W m⁻². The mixing layer height obtained from the Global Data Assimilation System (GDAS) 0.5° × 0.5° using HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory Model) closely follows this variation in
3 METHODOLOGY AND TOOLS

3.1 Organic Carbon (OC) and Elemental Carbon (EC) Measurements

The abundances of carbonaceous species (OC and EC) are measured hourly by an online EC-OC analyser (Sunset Lab, USA) based on the NIOSH 5040 (National Institute for Occupational Safety and Health) temperature protocol with thermo-optical transmittance (TOT) for charring correction. The instrument reports OC and EC concentrations utilising both thermal and optical properties. At the end of every run, the instrument is calibrated using a known amount of methane gas. External standardisation is done by introducing a known amount of sucrose in the filter and ensuring that the solar radiation and temperature and ranges from 584 m a.g.l. to 2056 m a.g.l. Wind speed attains a value as low as 1.9 m s\(^{-1}\) in September and as high as 3.6 m s\(^{-1}\) during April and May.
the detection is within an accuracy of 5%. More details on instrument, methodology, and calibration can be found in Birch and Cary (1996) and Srivastava and Naja (2021).

### 3.2 Equivalent Black Carbon (eBC) and Carbon Monoxide Measurements

The eBC measurements were made using an Aethalometer (AE-42), which measures the mass concentration based on the optical attenuation of a light beam at seven wavelengths. Since the ambient pressure at the site is lower than the standard pressure, the measured values of eBC by the instrument were corrected for standard temperature and pressure (STP) using the corrections given by Moorthy et al. (2004). Corrections to consider multiple scattering, loading, and shadowing effects have been done following the methods described by Drinovec et al. (2015) and Weingartner et al. (2003), respectively. Further details on these can be found in Srivastava et al. (2022). The data is additionally subjected to three-sigma outlier removal every ten minutes and then every hour to reduce noise. The uncertainty in the eBC measurement ranges between 20–30% after the due application of these corrections (Moorthy et al., 2007; Müller et al., 2011; Joshi et al., 2020). It is to be noted here that the reference to BC from Aethalometer measurements as eBC in this paper is made following the recommendations from Petzold et al. (2013). Importantly, the conversion of the absorption coefficient to eBC is done using monthly site-specific mass absorption cross-sections (MAC) as determined in Srivastava et al. (2022). These are provided for reference in Supplementary Table S2.

CO observations are made using an instrument (Picarro G2401) based on the cavity ring-down spectroscopy (CRDS) technique. The sensitivity of this system is higher than the conventional non-dispersive infrared or Fourier transform infrared spectroscopy techniques (Bitter et al., 2005). It can measure gases in parts per billion with high accuracy and with a very fast response (over a time scale of seconds). More details about the calibration and instrument can be found in Chandra et al. (2016). Horiba APMA 370 trace gas analyser (Kato, 2006) also operated at the site during 2014–2015. So, a regression between Picarro and Horiba was used to get CO from Horiba wherever CO from Picarro was not available. For consistency and noise reduction, the data collected at each second interval were averaged first to 1 minute after 3 sigma filtration. It was then averaged over ten minutes and finally, the hourly averaged concentrations were used in the final analysis. The CO data is used in the study to assist in the segregation of POC and SOC.

### 3.3 Trajectory Model

Concentration-weighted trajectory (CWT) gives the relative contribution of the most probable regions responsible for the long-range pollutant transport to the receptor site (Wang et al., 2009). Hence, to estimate the influence of transported aerosols in this study, endpoints of 5-day-backward trajectories for 5 particles (covering the four corners and one centre position for a 0.5° × 0.5° grid box centred at the observation site i.e., 29.4°N, 79.5°E) are calculated at 1000 m a.g.l. from the observational site using the HYSPLIT (Draxler and Hess, 1998) for the whole period of 2014–2017. Meteorology parameters required for input are taken from 0.5° × 0.5° GDAS archived at a 6-hourly interval. The residence time in each cell is weighed with the observed concentrations at the receptor site. Thus, the average weighted concentration $C_{ij}$ in the $ij$th cell is given as:

$$C_{ij} = \frac{1}{M} \sum_{l=1}^{M} c_i \tau_{ij}$$

(1)

where $l$ denotes the index of the trajectory, $M$ is the total number of trajectories, $c_i$ is the concentration observed at the site on the arrival of trajectory $l$, $\tau_{ij}$ represents the time spent in the $ij$th cell by trajectory $l$.

### 3.4 Radiative Forcing Estimates

To estimate the impact of eBC together with its fossil fuel and biomass fractions, on aerosol radiative forcing (ARF), we first use an aerosol optical model: Optical Properties of Aerosols and Clouds (OPAC, Hess et al., 1998) to obtain the optical properties such as aerosol optical depth.
(AOD), single scattering albedo (SSA), asymmetry function and angstrom exponent. These optical properties are then fed to the Santa Barbara Discrete Ordinate Atmospheric Radiative Transfer model (SBDART, Ricchiazzi et al., 1998) for ARF estimation. OPAC and SBDART have been widely used for ARF estimation in former studies (Moorthy et al., 2009; Kumar et al., 2011; Gogoi et al., 2017; Srivastava et al., 2021). The ARF estimation accuracy of the method is reported to be ± 2 W m–2 (Satheesh and Srinivasan, 2006).

4 RESULTS AND DISCUSSIONS

4.1 Source Identification Using Variations in Angstrom Exponent and OC/EC Ratio

Before making a quantitative assessment, a qualitative assessment is made to identify the sources of black carbon and we derived α in three different wavelength ranges—short: (370–520 nm), long: (660–950 nm), and total: (370–950 nm). Fig. 2 shows the percentage frequency distribution of α derived in these three wavelength ranges during four seasons. The α values lying in the range of 0.75–1.25 have the maximum frequency of occurrence. Traffic or diesel emissions have α values between 0.8 and 1.1 (Sandradewi et al., 2008). Thus, the highest occurring α, which is close to 1 and which is more pronounced in the longer wavelength range (Fig. 2(b)), indicates an overall dominance of fossil fuel burning. Higher α values, which are greater than one, occur during spring and winter in all the wavelength ranges (Fig. 2(c)). These values are relatively higher in the short wavelength range (370–520 nm). Such higher α values are observed in the case of emissions from biomass burning due to absorption by organic compounds in the ultraviolet and lower visible wavelengths (Kirchstetter et al., 2004; Day et al., 2006; Sandradewi et al., 2008; Titos et al., 2017).

Additionally, OC/EC ratios are also used to identify the sources at the site. The ratio of monthly averaged OC to that of EC varies between 2.7 to 4.4 over this region. Higher ratios of 4.1, 3.8, and 3.5 are observed in April, May, and June and have been found to be usually associated with large-scale biomass burning in northern India, due to crop-residue burning and forest fires purposes (Srivastava and Naja, 2021). The ratios of 3.6, 3.6, and 4.3 are observed in November, December, and January due to burning for the heating. Such higher ratios have also been observed in an urban environment in Helsinki, Finland (Saarikoski et al., 2008), remote high-altitude regions of Indian Himalayas (Srivastava et al., 2021), and Kumasi, Ghana (6°15′N, 1°15′W) (Srivastava et al., 2021).

Fig. 2. Seasonal variations in the percentage frequency distribution of angstrom exponents for (a) lower (370–520 nm), (b) higher (660–950 nm), and (c) total (370–950 nm) wavelengths.
Mt. Abu and Manora Peak (Ram et al., 2008), rural sectors of Indo-Gangetic Plains (Saud et al., 2013). The lower ratios (< 3) in other months denote a greater association with the burning of fossil fuel (Khan et al., 2012; Tiwari et al., 2013; Safai et al., 2014). Additionally, the OC/EC ratios greater than 2 are shown to be associated with the existence of higher secondary organic aerosols (Chow et al., 1996). Thus, these OC/EC ratios indicate the presence of secondary aerosol formation in the region which may be particularly high during the springtime. Both α and OC/EC ratios indicate the influence of biomass emission, fossil fuel sources, and the presence of SOC. Hence, we evaluate their contributions in the subsequent sections.

4.2 Source-Wise Quantification of Aerosols

4.2.1 Determination of primary and secondary organic carbon (POC and SOC)

To determine POC and SOC, we employ measurements from the online OC-EC analyser with the NIOSH technique and the EC tracer approach. With the transmittance-based charring corrections, it is demonstrated that accurate SOC calculation using EC-based tracer methods is independent of temperature protocols (EUSAAR, IMPROVE-A, NIOSH) (Cheng et al., 2014). A crucial step in this EC tracer method is the determination of primary OC/EC ratio i.e., [OC/EC]pri. Different methods are used in the literature to determine [OC/EC]pri as this ratio changes greatly according to the sources and modes of combustion. To obtain [OC/EC]pri, Cabada et al. (2004), for instance, specifically calculated the period of primary and secondary emissions. Lin et al. (2009) utilised regression excluding the rain period to get [OC/EC]pri. Ram et al. (2008), Safai et al. (2014), and Mishra and Kulshrestha (2021) used seasonal OC/EC minimum ratio as [OC/EC]pri. In contrast, Yu et al. (2021) employed a bottom-up approach whereas Yao et al. (2020) used the minimum regression square approach. In the absence of any uniform or standard methodology, the amount of the SOC and POC so computed can vary depending on the approach used, leading to ambiguity in subsequent comparisons. We thereby apply four approaches to determine [OC/EC]pri in the EC tracer method. The aim here is to use the popular methods currently used in the community, apply them to this site and intercompare them at different temporal scales and during biomass emissions for similarities and dissimilarities. The four approaches are described in detail in Section S1 and are compiled in Table 1 for quick reference. Briefly, TEN calculates the lowest 10 percentile as the [OC/EC]pri. REG estimates the regression slope between OC and EC for [OC/EC]pri. CAB also runs on the same principle as REG but segregates the period of primary emissions. In the case of MRS, the diurnal minimum of the determination coefficient (r²) between EC and hypothetical SOC values is estimated to get the [OC/EC]pri.

The application of MRS requires the use of a monthly dataset. Hence, to maintain consistency in [OC/EC]pri calculation for four methods and to incorporate monthly variations better, we estimate the monthly [OC/EC]pri for the 2014–2017 period and then estimate SOC and POC from hourly EC-OC data for any given method. The value of [OC/EC]pri thus obtained from these methods are given in the Supplementary Table S1. Here, Table 3 shows the averaged seasonal variation in POC, and SOC obtained using four methods (MRS, CAB, TEN and REG), and Table 2 provides their monthly values.

Agreeably in all the methods, the annual POC concentration (> 4.7 µg m⁻³) is higher than SOC concentrations (< 3.9 µg m⁻³), though in a few months, SOC is higher. Similarly, the annual POC/OC% (56–80%) is also higher than SOC/OC% (20–44%). This is consistent with a general prevalence of lower OC/EC ratios (< 3), discussed previously. This suggests that primary emissions dominate this region in comparison to secondary sources. Due to reduced concentrations seen throughout the year.

Table 1. Summary of the four methods used for SOC segregation along with their indicative references. TEN, REG, CAB, and MRS are defined in Section 4.2.1.

<table>
<thead>
<tr>
<th>Method name</th>
<th>Methodology</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEN</td>
<td>10 percentiles</td>
<td>Kaskaoutis et al. (2020)</td>
</tr>
<tr>
<td>REG</td>
<td>Slope, intercept (all data)</td>
<td>Lin et al. (2009)</td>
</tr>
<tr>
<td>CAB</td>
<td>Slope, intercept (all data – rain – night [19:5-hours] – r² &gt; 0.5 [eBC vs. CO])</td>
<td>Cabada et al. (2004)</td>
</tr>
<tr>
<td>MRS</td>
<td>Diurnal [min {r² (EC vs. possible SOC)}]</td>
<td>Wu et al. (2019)</td>
</tr>
</tbody>
</table>
Table 2. Monthly and annual averaged values of POC and SOC using the four methods.

<table>
<thead>
<tr>
<th></th>
<th>SOC (µg m⁻³)</th>
<th></th>
<th>POC (µg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MRS</td>
<td>REG</td>
<td>CAB</td>
</tr>
<tr>
<td>Jan</td>
<td>3.9 ± 3.8</td>
<td>3.5 ± 4.0</td>
<td>3.6 ± 4.2</td>
</tr>
<tr>
<td>Feb</td>
<td>3.1 ± 2.2</td>
<td>1.9 ± 2.0</td>
<td>2.3 ± 2.0</td>
</tr>
<tr>
<td>Mar</td>
<td>6.0 ± 4.3</td>
<td>2.3 ± 1.9</td>
<td>5.1 ± 3.2</td>
</tr>
<tr>
<td>Apr</td>
<td>7.8 ± 7.7</td>
<td>6.2 ± 7.0</td>
<td>6.2 ± 7.0</td>
</tr>
<tr>
<td>May</td>
<td>4.6 ± 4.8</td>
<td>3.5 ± 4.6</td>
<td>4.2 ± 4.6</td>
</tr>
<tr>
<td>Jun</td>
<td>4.3 ± 2.8</td>
<td>2.1 ± 2.8</td>
<td>4.5 ± 2.9</td>
</tr>
<tr>
<td>Jul</td>
<td>1.9 ± 1.1</td>
<td>0.8 ± 0.6</td>
<td>–</td>
</tr>
<tr>
<td>Aug</td>
<td>1.8 ± 1.2</td>
<td>1.0 ± 0.8</td>
<td>–</td>
</tr>
<tr>
<td>Sep</td>
<td>1.8 ± 1.1</td>
<td>0.9 ± 0.7</td>
<td>3.2 ± 1.5</td>
</tr>
<tr>
<td>Oct</td>
<td>2.2 ± 2.2</td>
<td>1.4 ± 1.6</td>
<td>1.8 ± 2.0</td>
</tr>
<tr>
<td>Nov</td>
<td>3.4 ± 3.2</td>
<td>2.4 ± 3.7</td>
<td>–</td>
</tr>
<tr>
<td>Dec</td>
<td>3.2 ± 2.2</td>
<td>1.5 ± 1.8</td>
<td>1.7 ± 1.7</td>
</tr>
<tr>
<td>Annual</td>
<td>3.9 ± 4.1</td>
<td>2.4 ± 3.5</td>
<td>3.9 ± 3.7</td>
</tr>
</tbody>
</table>

The rainy season of summer monsoons and early autumn, POC concentrations are at their seasonal maximum in the spring and winter. Additionally, seasonally, all four approaches cogently demonstrate that the largest SOC concentration is in spring. Higher solar flux and higher temperature (Fig. 1(c)) in this season, which result in higher VOCs along with enhanced biomass burning as also shown by higher OC/EC ratio (> 3) earlier, is the most likely reason for this enhanced SOC concentration (Ram et al., 2008; Safai et al., 2014).

Although all four approaches agree that POC dominates this region on a yearly basis and that SOC peaks seasonally in the spring, they each exhibit some variances. The following are the variations between the four methods. In MRS, CAB, and TEN, the average SOC concentration is close to ~3.9 µg m⁻³, however, it is as low as 2.4 µg m⁻³ in REG. The methods also exhibit a larger range in POC concentration, with MRS and TEN reporting annual average POC of 4.7–4.8 µg m⁻³, CAB reporting ~6 µg m⁻³, and REG reporting ~8 µg m⁻³. Furthermore, REG exhibits a higher sensitivity towards POC and shows a consistently high POC/OC% (~80%). Ram et al. (2008) also reported such bias while using regression slope (OC vs. EC).

The seasonally averaged diurnal variations of POC and SOC from four methods are shown in Fig. 4. It is evident that POC follows a unimodal diurnal variation during four seasons, except in
monsoon, with a noontime maximum and a higher diurnal amplitude in winter and spring. The lack of trend in monsoon is a direct result of heavy precipitation in this period. Otherwise, EC and OC are also found to follow this same unimodal variation. This variation is due to an interplay of boundary layer height and valley breeze. The daytime upslope winds flush the pollutants to the site alongside higher daytime boundary layer height. While the evening/night-time downslope winds bring the pollutant levels down with the lower boundary layer height (Sarangi et al., 2014; Joshi et al., 2016; Srivastava and Naja, 2021). In contrast, a bimodal diurnal variation with morning and evening peaks in POC and SOC is reported by an urban site in Pune owing to the fumigation effect (Safai et al., 2014).

Unlike the case of POC, the noon peak in the diurnal variation of SOC is not prominent, except in spring. The highest noon time rise is observed during spring in all the methods. It is also found that the variation of SOC follows the diurnal variation in OC/EC (Fig. S1). Many other studies have also reported the covariation of SOC with OC/EC ratio and O₃ (Cabada et al., 2004, Safai et al., 2014). The covariation of SOC with O₃ can be explained by the fact that the oxidation of VOCs by O₃ is one of the important pathways of SOC formation (Lin et al., 2009). It has been shown earlier (Kumar et al., 2010) that the photochemical oxidation is low at the present observation site during the daytime. Thus, the observed daytime lower concentration of SOC is in accordance with this lower photochemical oxidation. Further, both POC and SOC show a higher diurnal amplitude in spring in all four methods. This rise in the amplitude during spring is linked to the increased solar flux and higher boundary layer height in the daytime which supports both, the upward lift of pollutants from the low-lying polluted regions of the IGP (Sarangi et al., 2014; Srivastava and Naja, 2021) and an increased photo-oxidation (Kumar et al., 2010).

We find that all the methods agree in capturing the annual averaged variations, diurnal variations, and in showing high SOC in spring and an overall low concentration in summer-monsoon. However, their relative concentrations are different at monthly scales and in their diurnal amplitudes. These differences are inherently linked to the procedures adopted in the methods. Further, methods like TEN, REG, and CAB do not provide a uniform and quantifiable way of determining POC and

![Fig. 4. The diurnal variations in SOC and POC obtained using MRS, CAB, TEN, and REG methods averaged for the four seasons during 2014–2017. Error bars represent one standard deviation from the mean.](image)
SOC as different studies have used different periods/conditions for obtaining $[\text{OC/EC}]_{\text{pri}}$. The percentiles used for finding $[\text{OC/EC}]_{\text{pri}}$ can also range anywhere from 5 to 25 percentiles and may yield larger errors (Wu and Yu, 2016). Yao et al. (2020) compared SOC from MRS and regression over 20% dataset and found that MRS gave smaller errors. We also found that MRS includes the diurnal variations too while selecting the primary period. More importantly, it presents a uniformly applicable and quantifiable way of determining POC and SOC fractions. Nevertheless, in all our subsequent analyses, we continue to use POC and SOC from all the methods to keep a check on their differences.

4.2.2 eBC from fossil fuel combustion and biomass burning

The methodology to segregate eBC to fossil fuel (eBCff) and biomass (eBCbb) components is given in the Supplementary Section S2. The diurnal variations of eBC, eBCff and eBCbb, are shown in Fig 5. The concentrations exhibit a unimodal nature. The diurnal amplitude is somewhat lesser in the case of eBCbb which is discussed later. Such unimodal diurnal variation is expected for a cleaner site, where the concentrations are largely governed by the changes in the boundary layer height. The maximum eBC concentrations are observed in the afternoon when the boundary layer is fully evolved, and it brings the pollutants from the sources in the low-altitude regions. Such variations peaking during noontime at this site is in contrast with the bimodal diurnal variations observed at low-lying urban sites of Pantnagar (Joshi et al., 2016), Delhi (Tiwari et al., 2013) and Ahmedabad (Rajesh and Ramchandran, 2017). Furthermore, at these urban sites, eBCff shows a higher contribution during the night and early morning while a higher contribution from eBCbb is found during the morning and evening hours.

It is also observed that the differences in the average diurnal amplitude of eBCff and eBCbb are significantly lesser, reaching a minimum (0.17–0.33 $\mu$g m$^{-3}$), during April and May (Fig. S3). The percentage difference between eBCbb and eBCff drops to the lowest value of 9–32% in April–May. This signifies the relative importance of biomass emissions at a diurnal scale especially during the spring months. This increased influence of biomass emissions also reflects in the monthly concentrations and is consistent with the increased fire counts in the Northern Indian region (Fig. 6). Oct–Nov is also a fire period in the region as shown by fire count data. Additionally, as already

![Fig. 5. Diurnal variations of eBC and its fossil fuel (eBCff) and biomass burning (eBCbb) components averaged monthly during 2014–17. Data counts for each month are also given.](image-url)
mentioned in Section 4.1 that burning for the heating purpose in cold winter is an important source of eBC during November–February as the boundary layer height is relatively low thus increasing the influence of more local emissions (Srivastava and Naja, 2021).

Fossil fuel burning fraction (eBCff) closely follows the monthly variation in ambient eBC in general (Fig. 6). The annually averaged fossil fuel component is higher than the biomass component with an eBCff of 1.53 ± 1.3 µg m\(^{-3}\) and eBCbb of 0.44 ± 0.52 µg m\(^{-3}\). This implies that the contribution of eBCff is ~3.5 times higher than that of eBCbb annually. Percentagewise, the contribution of fossil fuel (eBCff) is dominant (67–90%) when compared with biomass burning (10–33%) in both monthly (Table 3) and diurnal scales (Fig. S2). This indicates that the emissions from sources such as automobile and industrial combustion contribute much more than biomass burning. Nainital is a hill station and hence attracts a large flux of tourists. As a result, influences of vehicular emissions could become an important source of eBC at the site.

Fig. 6. Boxplot showing annual variations in monthly averaged eBC, eBCff, and eBCbb concentration during 2014–2017. In boxplots, the lower and upper edges of the boxes represent the 25th and 75th percentiles, respectively. The whiskers below and above are the 10th and 90th percentiles. The triangle, circle, and square symbols inside the box represent the mean of eBC, eBCff, and eBCbb and the horizontal solid lines inside the box represent the median. The error bars represent one standard deviation from the mean. MODIS fire counts in the region 24–34°N, 70–90°E are also shown in the secondary y axes.

Table 3. Monthly averaged values of observed eBC, eBCff, eBCbb, and the percentage contribution of eBCff and eBCbb to eBC.

<table>
<thead>
<tr>
<th>Month</th>
<th>eBC (µg m(^{-3}))</th>
<th>eBCff (µg m(^{-3}))</th>
<th>eBCbb (µg m(^{-3}))</th>
<th>%BCff</th>
<th>%BCbb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan</td>
<td>1.72 ± 1.26</td>
<td>1.20 ± 1.04</td>
<td>0.52 ± 0.47</td>
<td>69 ± 19</td>
<td>31 ± 19</td>
</tr>
<tr>
<td>Feb</td>
<td>2.61 ± 1.93</td>
<td>2.11 ± 1.78</td>
<td>0.50 ± 0.38</td>
<td>77 ± 15</td>
<td>23 ± 15</td>
</tr>
<tr>
<td>Mar</td>
<td>2.10 ± 1.79</td>
<td>1.72 ± 1.60</td>
<td>0.38 ± 0.35</td>
<td>79 ± 12</td>
<td>21 ± 12</td>
</tr>
<tr>
<td>Apr</td>
<td>2.53 ± 1.75</td>
<td>1.68 ± 1.31</td>
<td>0.85 ± 0.92</td>
<td>67 ± 21</td>
<td>33 ± 21</td>
</tr>
<tr>
<td>May</td>
<td>2.59 ± 1.58</td>
<td>1.90 ± 1.14</td>
<td>0.69 ± 0.74</td>
<td>74 ± 16</td>
<td>26 ± 16</td>
</tr>
<tr>
<td>Jun</td>
<td>2.48 ± 1.26</td>
<td>2.09 ± 1.11</td>
<td>0.39 ± 0.43</td>
<td>84 ± 14</td>
<td>16 ± 14</td>
</tr>
<tr>
<td>Jul</td>
<td>0.80 ± 0.61</td>
<td>0.72 ± 0.60</td>
<td>0.08 ± 0.07</td>
<td>86 ± 14</td>
<td>14 ± 14</td>
</tr>
<tr>
<td>Aug</td>
<td>0.81 ± 0.64</td>
<td>0.72 ± 0.61</td>
<td>0.09 ± 0.13</td>
<td>86 ± 13</td>
<td>14 ± 13</td>
</tr>
<tr>
<td>Sep</td>
<td>1.23 ± 0.63</td>
<td>1.12 ± 0.61</td>
<td>0.11 ± 0.14</td>
<td>90 ± 12</td>
<td>10 ± 12</td>
</tr>
<tr>
<td>Oct</td>
<td>1.67 ± 1.00</td>
<td>1.35 ± 0.89</td>
<td>0.31 ± 0.31</td>
<td>80 ± 14</td>
<td>20 ± 14</td>
</tr>
<tr>
<td>Nov</td>
<td>1.77 ± 1.19</td>
<td>1.34 ± 1.02</td>
<td>0.43 ± 0.32</td>
<td>74 ± 14</td>
<td>26 ± 14</td>
</tr>
<tr>
<td>Dec</td>
<td>1.83 ± 1.32</td>
<td>1.40 ± 1.21</td>
<td>0.43 ± 0.35</td>
<td>72 ± 20</td>
<td>28 ± 20</td>
</tr>
<tr>
<td>Annual</td>
<td>1.97 ± 1.54</td>
<td>1.53 ± 1.30</td>
<td>0.44 ± 0.52</td>
<td>77 ± 17</td>
<td>23 ± 17</td>
</tr>
</tbody>
</table>
The seasonal variation in the concentrations and percentage contributions of eBC_f and eBC_bb are shown in Fig. S4. The seasonal average concentrations arising from both fossil fuel (1.3 ± 1.1 µg m⁻³) and biomass (0.2 ± 0.3 µg m⁻³) components of eBC are minimum during the monsoons (Fig. S4) which is consistent with the impact of the heavy precipitation during this period (Fig. 1(c)). Seasonally, the lowest eBC_bb percentage of ~15% is also observed during monsoons resulting as a direct consequence of the least fires in this period, which is also evidenced from Fig. 6. These results thus hereby quantify the temporal variation of emission due to the burning of fossil fuel and biomass. We now utilise these observations to estimate their impacts on radiative forcing.

### 4.2.3 Aerosol radiative forcing (ARF) due to eBC, eBC_f, and eBC_bb

Daily RF calculations are performed using the method prescribed in Section 3.4. These calculations are made in the wavelength region: 0.25–4.0 µm, for the whole year at hourly intervals in three categories namely (i) diurnal (0600–1800 hours) (ii) morning (0600–0900 hours) and (iii) afternoon (1400–1700 hours), for both with and without aerosols (separately for eBC_f and eBC_bb).

The diurnally averaged aerosol radiative forcing calculated at the top of the atmosphere (TOA), surface (SUR), and atmosphere (ATM) obtained for eBC_f and eBC_bb are shown in Fig. 7. The magnitude of diurnally averaged TOA, SURF, and ATM forcing are 6.8 ± 7.5, –33.5 ± 13.3, and 40.3 ± 18.6 W m⁻² for eBC, respectively. Further analysis reveals that the maximum fraction of RF comes from the fossil fuel fraction for TOA, SURF, and ATM forcing (5.9 ± 7.2, –31.7 ± 12.6, and 37.6 ± 17.42 W m⁻²) when compared with that from biomass fraction (3.7 ± 6.4, –27.3 ± 10.6 and 31.0 ± 14.4 W m⁻²), respectively. It suggests that the fossil fuel component leads to about 16.4%, 13.3%, and 32.0% higher radiative forcing than that from biomass fraction at ATM, SURF, and TOA, respectively. This implies that reduction in fossil fuel combustion is more effective in mitigating the adverse effect of positive atmospheric radiative forcing over this region.

Further, it is also evident that the afternoon RF is significantly higher in eBC_f at TOA (6.3 W m⁻²), SURF (–13.4 W m⁻²), and ATM (19.8 W m⁻²) than in the morning. Similarly, higher afternoon RF is also seen for eBC_bb at TOA (4.2 W m⁻²), SURF (–8.8 W m⁻²), and ATM (13.0 W m⁻²) than in the morning. Thus, the results show less effect of biomass in noon time and further highlight that the emission from fossil fuel is of much greater concern. Moreover, the results underline the importance of afternoon radiative forcing at the site. Previous study has shown that atmospheric radiative forcing may increase by 10–16% when aerosol diurnal variations are considered (Reddy et al., 2015). This also shows that incorporating high-resolution measurements is particularly essential while studying aerosol-radiation interaction over high-altitude Himalayan sites.

![Fig. 7. Diurnally averaged (0600–1800 hours), morning (or forenoon -fn: 0600–0900 hours) and afternoon (an: 1400–1700 hours), clear-sky shortwave (0.25–4.0 µm) direct aerosol radiative forcing (W m⁻²) at the surface (SUR), in the atmosphere (ATM) and at the top of the atmosphere (TOA) for eBC_f and eBC_bb.](image-url)
4.3 Correlation of Carbonaceous Aerosols and Influence of Meteorological Parameters

Fig. 8 shows the correlation of POC and SOC concentrations with eBC, eBC\textsubscript{bb}, eBC\textsubscript{ff}, and boundary layer height. It is found that eBC\textsubscript{ff} exhibits a good positive correlation ($r^2 > 0.5$ and slope $\geq 1$) with POC derived from all four methods (three methods are given in Supplementary Fig. S5). On the contrary, the correlation between eBC\textsubscript{ff} and SOC is lower ($r^2 < 0.1$ and slope $< 0.2$) in all the methods. This is as expected since both POC and eBC\textsubscript{ff} are emitted primarily from incomplete combustion as opposed to SOC. Additionally, the present site is a high-altitude site with mostly vehicular emission sources in its proximity. These are usually diesel- and gasoline-powered vehicles which are reported to have low OC/EC ratios (~1–4.2) and higher POC content (Schauer \textit{et al.}, 2002; Pipal \textit{et al.}, 2014; Safai \textit{et al.}, 2014). Moreover, these results enforce confidence in the segregation schemes employed since we arrive at the expected conclusions using two independent segregation methodologies: optical (eBC\textsubscript{bb} and eBC\textsubscript{ff}) and thermal (POC and SOC). These results are also strengthened by a higher correlation of POC found with eBC\textsubscript{ff} compared to SOC.

For correlations between eBC\textsubscript{bb} and POC-SOC, we found that 95 percentiles of eBC\textsubscript{bb} data lie below 1.5 $\mu$g m$^{-3}$ and therefore we show here the eBC\textsubscript{bb} data between 0–1.5 $\mu$g m$^{-3}$ instead of the full range (0–3 $\mu$g m$^{-3}$) to avoid the impact of outliers. Results show that in general, the correlation of eBC\textsubscript{bb} with POC was lower than that with SOC for all the methods. In fact, for MRS, TEN, and REG, the $r^2$ is greater than 0.9 between eBC\textsubscript{bb} and SOC while $r^2$ is lesser than 0.6 for regression between eBC\textsubscript{bb} and POC from MRS, TEN, and CAB, thus, implying that the secondary organic content is better correlated with the biomass burning fraction. This happens because biomass burning is known to be associated with higher volatile organic compounds and higher OC/EC (>4), that oxidise and condense to SOC as they age reaching the present site (Zhang \textit{et al.}, 2007; Ram \textit{et al.}, 2010). It is also found that the SOC has a higher correlation ($r^2 \sim 0.7$) with mixing layer height compared to that with POC ($r^2 < 0.3$ for three methods) indicating that the SOC formation is linked more to the rise in the mixing layer height compared to POC. The results, therefore, highlight that the POC emissions at the site are associated with eBC\textsubscript{ff} emissions while the SOC emissions are associated with eBC\textsubscript{bb} and higher mixing layer height.

We also studied the variation of eBC\textsubscript{ff}, eBC\textsubscript{bb}, POC, and SOC with the meteorological variables (temperature, wind speed, relative humidity, solar radiation, and rain) (Supplementary Fig. S8). Diurnally, during the dry months (RH < 60%, rainfall < 47 mm) from October to May, we found that higher temperature, greater solar radiation, higher boundary layer height and lower wind speed supported a near-simultaneous unimodal daytime build-up of eBC\textsubscript{ff}, eBC\textsubscript{bb}, POC, EC, and OC. During nights, lower temperatures, reduced solar radiation, lower boundary layer height, and higher windspeed lead to better ventilation and hence lower concentrations of the species. The daytime covariation of OC and EC tends to get disrupted during April–May when SOC concentration rises with higher temperature, moderate humidity, and higher ozone fraction (Kumar \textit{et al.}, 2010; Sarangi \textit{et al.}, 2014; Srivastava and Naja, 2021). In these months, the daytime peak in OC and SOC concentration precedes that in EC and POC. The concentration of SOC dipped...
steeper than POC with higher RH and rain during the wet months (RH > 87%, avg rain > 430 mm) possibly due to the presence of water-soluble components. The results are in line with the previous analysis of BC, OC, and EC variations discussed in Joshi et al. (2020), Srivastava and Naja (2021), and Srivastava et al. (2022).

### 4.4 Source Region Identification

Fig. 9 shows the concentration-weighted trajectories of eBC averaged during four seasons of the 2014–2017 period. In general, the higher eBC concentrations are mainly associated with the air masses from the north-western regions of the IGP. The greatest contribution of these higher concentrations (> 2 µg m⁻³ shown in orange and red) is observed during spring followed by winter. These potential source zones lie coherently with the sources of fossil fuel combustion such as factories, power plants, and transportation activities which are located at the densely populated urban core of the IGP. However, these are relatively constant sources of emissions. The higher concentrations are also a result of the high fire events in IGP which are associated with the seasonal stubble burning especially in spring. Higher wind speed and greater convection during spring support the transport of pollutants even from far-off regions of the IGP to the site, despite its high altitude. Lower concentrations (≤ 2 µg m⁻³) observed during autumn are likely a result of the lower boundary layer height and lower wind speed (Fig. 1(c)) observed during this period. Additionally, the area of pollutant transport is the least during the summer monsoon, as this period is associated with heavy rain spells brought to the region by the southwest monsoon winds which are of the cleaner oceanic region. Much lesser concentrations (< 1.5 µg m⁻³) are associated with the air masses arriving from regions farther from India. The results thus reveal that even at this high altitude, the site is considerably affected by the transported pollutants from the north-western IGP region and biomass-burning events, especially during spring. We now assess the impact of such a biomass-burning event on carbonaceous aerosols in the next section.

### 4.5 Case Study – Influence of Biomass Burning on eBC, EC, OC, eBCbb, eBCff, POC, and SOC

Here, we analyse an event of rising fire emissions from 19 April 2016 to 04 May 2016 (Fig. 10). MODISv6.2 fire data (https://firms.modaps.eosdis.nasa.gov/) for the night-time (since it has greater sensitivity, Bhardwaj et al., 2016) with a confidence level greater than 80% is taken for
the region 24°N to 35°N and 70°E to 89°E. Backwards trajectories show that the air mass arrives at the site from the north-western region in both the low (22 April) and high (1 May) fire days. The systematic rise in fire events is followed by a rise in concentrations. OC concentrations on 30 April almost doubled from their concentrations on 22 April. The OC/EC ratios also rose from 4.6 to 7.9. When the fire counts on 22 April were lower than on 30 April, the SOC concentrations were also less than 10 µg m⁻³ in all the methods. As the fire counts gradually rose to as high as 257 on 01 May, simultaneously, the SOC concentration also crossed about 20 µg m⁻³ in all the methods. Similarly, the eBCbb concentration which is usually lower than the eBCff component at the site also enhanced to levels higher than those of eBCff with the rise in fire events.

Further, the magnitude of this rise in SOC with fire events varied in different methods (Fig. 10...
MRS and TEN showed greater sensitivity and the fraction of OC allotted to SOC is higher compared to POC. However, the difference in POC and SOC concentrations is comparatively lesser in CAB and REG during the fire events. Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation (CALIPSO) aerosol subtype imagery (Fig. S7(b)) during this period (01 May) around the site also reveals the presence of elevated smoke and polluted dust. However, such elevated smoke aerosols are not classified during the low fire period (22 May) (Fig. S7(a)). These results clearly emphasise the importance of episodic and variable biomass burning emissions in such high-altitude sites as they lead to significantly higher concentrations of carbonaceous aerosols.

5 CONCLUSIONS

To fill the knowledge gap in terms of high-resolution source apportionment studies, the in-situ simultaneous online observations of OC, EC, eBC, and CO were conducted at a high-altitude site in the Central Himalayas during the period of 2014–2017. The major conclusions from this study are summarised below:

1. The year-round diurnal variations in POC and SOC are estimated for the first time in the Central Himalayan region. Unlike SOC, POC with a significant unimodal diurnal variation is shown to dominate the OC concentration at the site.

2. It is shown that the fossil fuel component dominates the site throughout the year. Although the biomass-burning component dominates during spring, it remains lower than the fossil fuel component.

3. The difference in diurnal amplitudes of eBC<sub>f</sub> and eBC<sub>b</sub> is the least during spring (9–32%). This signifies the relative importance of consideration of biomass emissions at a diurnal scale.

4. Estimated radiative forcing due to fossil fuel component (eBC<sub>f</sub>) is shown to be ~3.5 times higher than that because of biomass burning component (eBC<sub>b</sub>). It is also shown that the radiative forcing during the afternoon plays a dominant role with 19.8 and 13.0 W m<sup>-2</sup> higher radiative forcing in eBC<sub>f</sub> and eBC<sub>b</sub> compared to the morning.

5. The correlation of carbonaceous aerosols with other pollutants shows that POC concentrations are well correlated with the eBC<sub>f</sub> while the SOC concentrations are more influenced by eBC<sub>b</sub> and higher mixing layer height.

6. CWT analysis and study of biomass burning events reveals that even at this high altitude, the site is appreciably affected by the transported pollutants from the north-western IGP region, especially during spring.

This study thus provides the first long-term diurnal-scale characterisation of carbon-based pollutants in an otherwise little-studied climatologically significant high-altitude region of the Central Himalayas. We envisage that these observations of the carbonaceous aerosols and their source characterization can serve as an important piece of the dataset and will be resourceful in formulating the mitigation policies, constraining radiation budget, studying their health and climatological impacts in the poorly studied and fragile region of the Central Himalayas.

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ADDITIONAL INFORMATION AND DECLARATIONS

Disclaimer
The authors declare that they have no conflict of interest.

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**Data Availability Statement**

All observational data used in this analysis are available at the ARIES data bank.

**Supplementary Material**

Supplementary material for this article can be found in the online version at https://doi.org/10.4209/aaqr.220381

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Validation of SOC estimation using OC and EC concentration in PM$_{2.5}$ measured at Seoul. 